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Lagosta, 9, I-20159 Milano (IT). **SIN XICOLA, Agustin**  
[ES/IT]; Via Bazzini, 19/b, I-20040 Carnate (IT).

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(74) Agents: **GIANNESI, Pier, Giovanni** et al.; Pirelli & C.  
S.p.A., 222, Viale Sarca, I-20126 Milano (IT).

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(71) Applicant (for all designated States except US): **PIRELLI**  
& C. S.P.A. [IT/IT]; 10, Via Gaetano Negri, I-20123 Mi-  
lano (IT).

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(72) Inventors; and

(75) Inventors/Applicants (for US only): **ARICO, An-**  
tonino, Salvatore [IT/IT]; Via SS 114 Km. 3.900, CPL  
Azzurra, 92, I-98125 Contesse (IT). **GULLO, Laura**,  
Rosalba [IT/IT]; Via Contesse 4, I-98125 Messina (IT).  
**LA ROSA, Daniela** [IT/IT]; Via Vico Arco, 7, I-98055  
Lipari (IT). **SIRACUSANO, Stefania** [IT/IT]; Via  
Regina Margherita, 21, I-98121 Messina (IT). **LOPES**  
**CORREIRA TAVARES, Ana, Berta** [PT/IT]; Piazzale

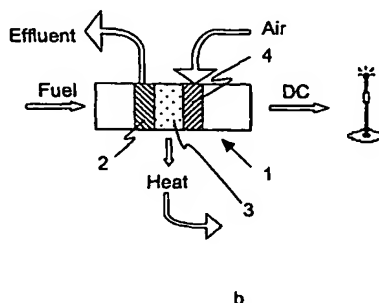
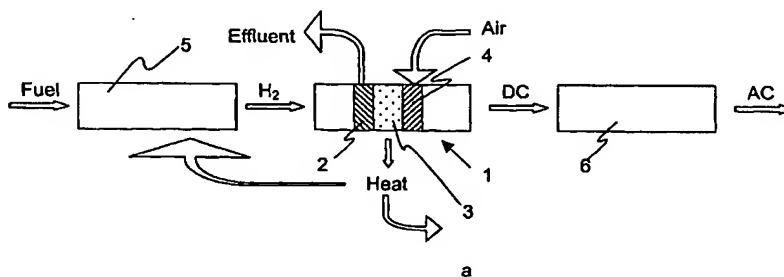
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(54) Title: CERAMIC ANODE SOLID OXIDE FUEL CELL



(57) Abstract: A solid oxide fuel cell including a cathode, at least an electrolyte membrane, and an anode comprising a ceramic material and an alloy comprising nickel and at least a second metal, said alloy having an average particle size not higher than 20 nm.

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## CERAMIC ANODE SOLID OXIDE FUEL CELL

The present invention relates to a solid fuel cell, to a cermet material, and to the process for the preparation of said cermet, and to a method for producing energy using such cell.

5 Solid-oxide fuel cells (SOFCs) convert chemical energy into electrical energy with high efficiency and low emission of pollutants. Although the introduction of a "green energy" might seem an attractive scenario, its implementation is beset with technical and economic difficulties.

10 The most common anodes materials for solid oxide fuel cells comprise nickel (Ni) cermets (ceramic and metallic composite materials) prepared by high-temperature calcination of NiO and ceramic powders, usually yttria-stabilized zirconia (YSZ) powders. These Ni-cermets perform with H<sub>2</sub> fuels and allow internal steam reforming of hydrocarbons if there is sufficient water in the feed to the anode. Because Ni catalyzes the formation of graphite fibers in dry methane, it is necessary to operate anodes at steam/methane ratios greater than 3, as from WO 00/52780 (in the name of Gas Research Institute).

15 S.J.A. Livermore et al. *Journal of Power Sources*, vol. 86 (2000), 411-416, refers to a cermet anode for SOFC made of nickel and ceria-gadolinia (CGO). This anode performs at 600°C using 10% H<sub>2</sub>/N<sub>2</sub> as the fuel.

20 A. Müller et al., Proc. of the 3rd European Solid Fuel Cell Forum, Nantes France, June 1998, 353-362, relate to a Ni-YSZ anode fuel cell. It is envisaged a degradation of the anode related to microstructural changes occurring during operation. The nickel particles have a mean diameter of about 0.5 µm, and are homogeneously distributed in the anode. After long term operation at high current density and fuel utilization (H<sub>2</sub>+H<sub>2</sub>O), the agglomeration of the nickel particles leads to a decrease of the amount of three-phase boundary (TPB), resulting in an increase in the anode losses.

25 A.C. Müller et al., HTMC IUPAC Jülich 2000 suggest that the degradation described by the previous document could be prevented by a multilayer anode whose divers layers differ in their microstructure to fulfill the locally different requirements for SOFC anodes. In particular, the content of Ni and the

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Ni particle size should increase from first layer (that in contact with the electrolyte) to last layer, thus increasing electronic conductivity, TEC (Thermal Expansion Coefficient) and porosity. The YSZ content should simultaneously decrease. The cermet samples were prepared by mixing 65-85 mol% NiO powder with YSZ powder and sintering them in air at 1300°C for 5 hours. The particle size of the metallic portion was 0.5-8 µm.

The use of nickel as the metallic component of a cermet anode is advantageous, but its performance drops in short time, especially when a dry hydrocarbon is the fuel, due to graphite formation.

R.J. Gorte et al., *Adv. Mater.*, 2000, vol.12, No. 19, 1465-1469, propose to substitute nickel with copper (Cu) in a cermet wherein the ceramic portion is YSZ. Other components, including ceria (CeO<sub>2</sub>), can be added to the metallic portion. In this configuration the role of CeO<sub>2</sub> is mainly to provide catalytic activity for the oxidation of hydrocarbons. As shown in Figure 4a of this paper, the cell prepared with Cu but without ceria exhibits poor performance at 700°C, especially when methane is used as fuel.

C. Lu et al., *High Temperature Materials, Proceedings volume 2002-5*, Ed. S.C. Singhal, Pacific Northwest National Laboratory, Richland, Washington, USA, relate to a Cu-SDC (samaria-doped ceria) anode composite cell performing H<sub>2</sub> and butene fuels at 700°C.

From the above studies, it results that copper alone cannot be an efficient substitute for nickel as its performance is insufficient, in particular with fuels such as dry hydrocarbons.

H. Kim et al., *J. Electrochem. Soc.*, vol.149 (3), A247-A250 (2002) examine the use of Cu-Ni alloys as anode component for the direct oxidation of methane in SOFC at about 800°C. The ceramic portion, which in this case is YSZ, is made by casting a tape with graphite pore formers over a green tape of YSZ without pore formers, firing the two-layered tape to about 1500°C. The porous anode layer was then impregnated with an aqueous solution of Ce(NO<sub>3</sub>)<sub>3</sub>·H<sub>2</sub>O and calcinated at about 500°C to decompose the nitrate ions and form CeO<sub>2</sub>. After the addition of ceria, the porous layer was impregnated

with a mixed, aqueous solution of  $\text{Cu}(\text{NO}_3)_2 \cdot \text{H}_2\text{O}$  and  $\text{Ni}(\text{NO}_3)_2 \cdot \text{H}_2\text{O}$  having the desired Cu:Ni ratio. Finally the wafer was again heated to about  $500^\circ\text{C}$  in air to decompose the nitrates and reduced in flowing  $\text{H}_2$  at about  $900^\circ\text{C}$ .

The Applicant has faced the problem of providing a solid oxide fuel cell which is able to show high efficiency and to maintain its performance over time, particularly in terms of a low overpotential in a wide range of temperatures. Moreover, the fuel cell should be able to show the above characteristics when fed with different fuels. Endurance of performance is particularly important when a dry hydrocarbon is used as fuel, since it tends to form graphite fibers on the metallic portion of the cermet anode, which eventually annihilate the fuel cell activity.

The Applicant has now found that by using a nickel alloy with one or more metals as metallic portion of a cermet anode, and by reducing the average size of the particles constituting said alloy, the resulting SOFC shows enduring efficiency when fuelled with different fuels, including hydrogen and hydrocarbons, in a wide range of operating temperatures, and particularly at low temperatures, namely from  $500^\circ\text{C}$  to  $700^\circ\text{C}$ . Particularly, when a dry hydrocarbon is used as fuel, deposition of graphite fibers is remarkably reduced. This result is particularly surprising since a reduction of the average particle size in the metallic component of the cermet would have been expected to increase the catalytic activity also with respect to those side reactions which cause formation of the graphite fibers.

The present invention thus relates to a solid oxide fuel cell including

- a cathode;
- at least an electrolyte membrane, and
- an anode comprising a ceramic material and an alloy comprising nickel and at least a second metal selected from aluminium, titanium, molybdenum, cobalt, iron, chromium, copper, silicon, tungsten, niobium, said alloy having an average particle size not higher than 20 nm.

Preferably the anode of the invention comprises an alloy wherein said alloy has an average particle size not higher than 16 nm. More preferably said average particle size is not lower than 1 nm.

5 The alloy of the anode of the invention can show a mean surface area higher than 20 m<sup>2</sup>/g, preferably higher than 30 m<sup>2</sup>/g, and more preferably higher than 40 m<sup>2</sup>/g.

Preferably in the anode of the invention the alloy has a second metal content of from about 1% by weight to about 99% by weight, more preferably, and even more preferably from about 40% by weight to about 60% by weight.

10 Preferably in the anode of the present invention the alloy has a nickel content of from about 1% by weight to about 99% by weight, more preferably from about 30% by weight to about 70% by weight, and even more preferably of about 50% by weight.

Preferably, said second metal is copper.

15 Said alloy can comprise an additional metal, for example, an element belonging to one of the classes from 3 to 13 of the periodic table of elements according to Chemical and Engineering News, 63(5), 27, 1985, lanthanides series included.

20 The ceramic material of the anode of the invention can be selected from yttria-stabilized zirconia (YSZ), cerium gadolinium oxide (CGO), samarium-doped ceria (SDC), mixed lanthanum and gallium oxides. Preferably the ceramic material is cerium gadolinium oxide (CGO).

The ceramic material of the anode of the present invention can show a particle size not higher than 50 nm, preferably from about 1 to about 25 nm.

25 Optionally, said ceramic material is doped with at least one cation selected from calcium, magnesium, strontium, lanthanum, yttrium, ytterbium, neodymium and dysprosium.

Optionally, the alloy of the invention comprises cerium oxide (CeO<sub>2</sub>), optionally added with additives like cobalt.

30 The solid oxide fuel cell according to the present invention can be operated in a wide range of temperatures, usually ranging from 450°C to 800°C,

and preferably from 500°C to 700°C

In another aspect the present invention relates to a cermet comprising an alloy having a particle size not higher than 20 nm.

Both the metallic and the ceramic portion of the cermet anode of the present invention can be prepared from the corresponding metal salts, which may be compounded in a solid solution of the oxides thereof.

In a further aspect the present invention relates to a process for preparing a cermet including a ceramic material and a metallic material comprising an alloy comprising nickel and at least a second metal selected from aluminium, titanium, molybdenum, cobalt, iron, chromium, copper, silicon, tungsten, niobium, said process comprising the steps of:

- a) producing a precursor of the metallic material;
- b) producing the ceramic material;
- c) combining said precursor and ceramic material to obtain a composite;
- d) reducing said composite

wherein step a) comprises the phases of

- a-1) dissolving a hydrosoluble salt of Ni and a hydrosoluble salt of a second metal in water;
- a-2) adding a chelating agent to the solution resulting from step a-1);
- a-3) adding an oxidizing agent to the solution resulting from step a-2);
- a-4) isolating said precursor.

Optionally, the pH of the solution resulting from phase a-2) is adjusted at a value higher than about 5.

Preferably, phase d) is carried out by hydrogen at a temperature ranging between about 400°C and about 1000°C, more preferably between about 500°C and about 800°C.

Step b) can include phases analogous to those from a-1) to a-4) of the process above, starting from the hydrosoluble salts corresponding to the ox-

ide of the desired ceramic material. Phase a-4) can be followed by a crystallization step, for example at a temperature ranging between about 200°C and about 700°C, more preferably between about 300°C and about 500°C.

Preferably, the oxides of the present invention are prepared starting from hydrosoluble salts of the desired metals which are dissolved in water and added with a chelating agent, for example, EDTA, oxalic, citric, acetic acid and the organic salts thereof, while maintaining the reaction mixture at a suitable pH, for example, higher than about 5.

Oxidation is then carried out, e.g. by addition of a peroxide, such as hydrogen peroxide, and co-precipitate of amorphous metal oxides is obtained.

This co-precipitate comprises very fine amorphous particles substantially free from any crystallographic ordering as revealed by XRD (X-ray diffraction) and TEM (transmission electron microscopy) analyses, as shown in the examples. The morphological and structural features obtained through this preferred method allow a superior extension of the three-phase boundary (TPB) zone, advantageous to the performance of the SOFC.

After thermal treatment of the precursor, in air or inert atmosphere, for example helium, a solid solution of the metallic oxides intimately admixed on an atomic scale, with fine particles size, is obtained. The particle size can range from about 3 to about 20 nm, preferably from about 4 to about 7 nm, more preferably of about 5 nm.

In the case the ceramic portion of the cermet anode according to the invention is prepared through the above mentioned process, crystallization of the amorphous oxide precursor, for example at a temperature ranging between about 200°C and about 700°C, more preferably between about 300°C and about 500°C, can yield a ceramic with small particle size, for example ranging between about 6 and about 2nm.

The preparation of the cermet anode, i.e. the material system comprising a metallic and a ceramic phase, can be carried out as follows. Amorphous mixed oxide precursor, obtained as said above, and a ceramic powder, preferably CGO or SDC, are admixed, and a slurry is prepared by dispersing the

reactants in an organic solvent, for example isopropanol, and further treated with ultrasounds. The mixture is heated for solvent evaporation, and a reduction, for example in H<sub>2</sub> atmosphere, is carried out while heating, for example at a temperature ranging between about 400°C and about 1000°C, more preferably between about 500°C and about 800°C.

A solid oxide fuel cell of the invention can be prepared by applying said slurry of composite on an electrolyte membrane comprising a ceramic material, for example, CGO, SDC or YSZ.

A cathode for the solid oxide fuel cell of the invention can comprise a perovskite such as La<sub>1-x</sub>Sr<sub>x</sub>MnO<sub>3-δ</sub>, for example can be a La<sub>0.6</sub>Sr<sub>0.4</sub>MnO<sub>3</sub>/CGO.

The solid oxide fuel cell according to the invention displays great flexibility in the choose of the fuel to be fed with. It can performs by feeding the anode with a fuel selected from hydrogen; an alcohol such as methanol, ethanol, propanol; a hydrocarbon in gaseous form such as methane, ethane, butene; carbon dioxide, carbon monoxide, natural gas, reformed natural gas, biogas, syngas and mixture thereof, either in the presence of water or substantially dry; or an hydrocarbon in liquid form, e.g. diesel, toluene, kerosene, jet fuels (JP-4, JP-5, JP-8, etc). Preferred by the present invention is substantially dry methane.

When a substantially dry fuel is fed to the anode, a direct oxidation is effected in the solid oxide fuel cell of the invention. In the case of dry methane, the reaction at the anode is the following



As already said above, the direct oxidation of a dry fuel such as a dry hydrocarbon yields coking phenomena (deposition of graphite fibers) at the metallic portion of the cermet thus exhausting the catalytic activity. The solid oxide fuel cell of the invention can perform by direct oxidation of a dry fuel.

In another further aspect, the present invention relates to a method for producing energy comprising the steps of:

- feeding at least one fuel into an anode side of a solid oxide fuel cell comprising an anode including a ceramic material and an alloy comprising nickel and at least a second metal selected from aluminium, titanium, molybdenum, cobalt, iron, chromium, copper, silicon, tungsten, niobium, a cathode and at least an electrolyte membrane disposed between said anode and said cathode;

- feeding an oxidant into a cathode side of said solid oxide fuel cell; and

- oxidizing said at least one fuel in said solid oxide fuel cell, resulting in production of energy.

The operating temperature of the solid oxide fuel cell of the invention can range from 450°C to 900°C, preferably from 500°C and 800°C.

An advantage provided by low operating temperatures, such those preferred by the present invention, is the reduction of NO<sub>x</sub> formation at the cathode. The formation of such undesired by-products is due to the reaction of the nitrogen present in the air fed at the cathode side, such reaction being related to temperature increase.

In case of operating with reformed fuel, the fuel is internally reformed at the anode side.

The invention will be further illustrated hereinafter with reference to the following examples and figures, wherein

- Figures 1a and 1b schematically illustrate fuel cell power systems;
- Figure 2 illustrates XRD patterns of (a) amorphous oxide precursor Ni<sub>0.58</sub>Cu<sub>0.42</sub>O, (b) crystalline oxide precursor Ni<sub>0.58</sub>Cu<sub>0.42</sub>O and (c) Ni<sub>0.58</sub>Cu<sub>0.42</sub> bulk alloy;
- Figure 3 shows temperature reduction profiles with H<sub>2</sub> for (a) CuO, (b) NiO and (c) Ni<sub>0.58</sub>Cu<sub>0.42</sub>O crystalline precursor;
- Figure 4 illustrates catalytic activity vs temperature profile for methane steam reforming experiments carried out for Ni<sub>0.58</sub>Cu<sub>0.42</sub> bulk alloy and Ni,Cu metallic mixture;
- Figure 5 shows XRD pattern of a Ni<sub>0.58</sub>Cu<sub>0.42</sub> (\*)-CGO (o) cermet;

- Figure 6 shows XRD patterns of (a) crystalline  $\text{Ni}_{0.5}\text{Cu}_{0.5}\text{O}$ -CGO composite after thermal treatment at  $500^{\circ}\text{C}$  and (b)  $\text{Ni}_{0.5}\text{Cu}_{0.5}$  (\*)-CGO (o) cermet after reduction at  $900^{\circ}\text{C}$ ; (#) corresponds to CuO phase;
- Figure 7 shows electrochemical polarisation curves for  $\text{Ni}_{0.58}\text{Cu}_{0.42}$ -CGO cermet anode/CGO electrolyte interface in dry  $\text{H}_2$  and dry  $\text{CH}_4$  in the temperature range between  $650^{\circ}$  and  $800^{\circ}\text{C}$ ;
- Figure 8 illustrates IR free electrochemical polarisation curves for  $\text{Ni}_{0.58}\text{Cu}_{0.42}$ -CGO cermet anode/CGO electrolyte interface in dry  $\text{H}_2$  and dry  $\text{CH}_4$  in the temperature range between  $650^{\circ}$  and  $800^{\circ}\text{C}$ ;
- Figures 9 illustrates a SEM micrograph of a  $\text{Ni}_{0.58}\text{Cu}_{0.42}$ -CGO anodic cermet layer of the invention, in cross-section;
- Figures 10a and 10b show TEM images of, respectively, amorphous and crystalline  $\text{Ni}_{0.58}\text{Cu}_{0.42}$ -CGO cermet according to the invention;
- Figure 11 show a low resolution TEM micrograph of  $\text{Ni}_{0.58}\text{Cu}_{0.42}$ -CGO anodic cermet layer, according to the invention, after 25 h at  $250\text{ mA cm}^{-2}$  in dry methane

Figures 1a and 1b schematically illustrate a solid oxide fuel cell power systems. The solid oxide fuel cell (1) comprises an anode (2), a cathode (4) and an electrolyte membrane (3) disposed between them.

In Figure 1a fuel generally a hydrocarbon, is fed to be converted into hydrogen as described, e.g., in "Fuel Cell Handbook", sixth edition, U.S. Dept. of Energy, 2002. Hydrogen is fed to the anode side of the solid oxide fuel cell (1). Cathode (4) is fed with air.

The fuel cell (1) produces energy in form of heat and electric power. The heat can be used in a bottoming cycle or conveyed to fuel reformer (5). The electric power is produced as direct current (DC) and may be exploited as such or converted into alternate current (AC) via a power conditioner (6).

Figure 1b shows a preferred embodiment of the invention. A substantially dry fuel is fed to the anode (2) where direct oxidation is effected. The heat can be used in a bottoming cycle. The direct current produced is exploited as such, for example in telecommunication systems.

In both the cases of Figures 1a and 1b, from anode (2) an effluent flows which can be composed by unreacted fuel and/or reaction product/s, for example water and/or carbon dioxide in the case of Figure 1b.

#### Example 1

##### Oxide precursor and alloy preparation

- a) NiCu alloys were prepared from reagent graded  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  and  $\text{Cu}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  (Aldrich 99.99). Stoichiometric amounts of the metal nitrates (2.86 g of  $\text{Cu}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ , 3.1 g of  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ) were dissolved in distilled water (50 ml) and then complexed at 60°C with an aqueous solution of oxalic acid (9.5 g in 200ml; Aldrich 99.99) at pH=6.5 adjusted with NaOH 0.1N. The molar ratio between complexing agent and the sum of the metal ions was 10. The complex formation was monitored by UV spectroscopy. The solution was heated to 80°C, and oxygen peroxide (400 ml, 20%, Carlo Erba) was then dropwise added until complete formation of a precipitate. The precipitate was filtrated, washed with distilled water, and dried at 120°C K for 12 hours.
- b) The powder obtained at step a) was then calcinated at 500°C in air for 0.5 hour, to yield a crystalline phase.
- c) The crystalline phase of step b) was heated at 500°C under  $\text{H}_2$  atmosphere ( $\text{H}_2$  for 30 min, 50 cc min<sup>-1</sup> g<sup>-1</sup> catalyst), in order to reduce the oxide phase to a metallic phase.

In order to verify the phase composition and structure at steps a), b) and c), the powders were analyzed by X-ray fluorescence (XRF) and X-ray diffraction (XRD) analyses.

XRF analysis (for composition) was carried out by Explorer Spectrometer (Bruker AXS, Germany) equipped with a Rh X-ray source. The instrument was equipped with 0.12° divergence collimator, LiF220 crystal analyzer and scintillation as well as proportional detectors.

XRD analysis (for structure and particle size determination) was carried out under Bragg-Brentano configuration with CuKalpha radiation with Xpert Diffractometer (Philips). The instrument was equipped with graphite mono-

chromator. The analysis range was selected from 5° to 100° 2 $\theta$ , the sweep rate was 1.5 ° min<sup>-1</sup>. Results are shown in Figure 2.

For each step product, the average particle size was calculated from XRD line broadening measurements using Scherrer equation. The results are set forth in Table 1, wherein the metal surface area was calculated from the particle size by the following formula:

$$\text{MSA (m}^2\text{g}^{-1}) = 6 \cdot 10^4 / (\rho \cdot d);$$

wherein  $\rho$  (g cm<sup>-3</sup>) is density and  $d$  (Å) particle size.

The formation of the metal solid solution was checked by XRD, monitoring the shifts on the diffraction peak assigned to the various reflections in particular the Ni (200) (JCPDS - ICDD data file, card n° 4-8509) and Cu (200) (JCPDS - ICDD data file, card n° 4-836) planes, and calculating the variation in the lattice parameter of the metallic alloy structure from Vegard law.

Table 1

Lattice parameter (a), particle size (d) and surface area (SA) of NiCuO<sub>x</sub> and NiCu phases

Phase / preparation step (ex. 1)	(Ni:Cu)	Lattice parameter $a_{\text{fcc}}/\text{\AA}$	Particle size $d/\text{nm}$	Surface area $\text{SA}/\text{m}^2 \text{g}^{-1}$
NiCuO <sub>x</sub> amorphous (step a)	90:10	-	< 1.5	-
	65:35	-	< 1.5	-
	58:42	-	< 1.5	-
NiCuO <sub>x</sub> crystalline (step b)	90:10	4.162	6.7	100.6
	65:35	4.178	4.1	164.4
	58:42	4.183	4.3	156.8
NiCu alloy (step c)	90:10	3.521	15.9	42.4
	65:35	3.549	13.4	50.3
	58:42	3.552	19.2	36.0

XRD analysis of the powder obtained from step a) did not show any important crystallographic reflection but only an amorphous scattering, as from Figure 2,a).

XRD analysis of the powder obtained from step b) showed the characteristic peaks of the faced centered cubic (fcc) structure of NiO shifted linearly as a function of the composition of the solid solution, as from Figure 2,b). No evidence of monocline CuO phase was observed indicating that Cu atoms occupy the same crystallographic positions of Ni in the fcc structure with a random distribution. No evidence of superlattice lines was detected.

XRD analysis of the powder obtained from step c) showed for the various compositions only the typical diffraction peaks of the fcc structure, as from Figure 2,c). The lattice parameter varied linearly between pure Ni and Cu metals as a function of relative composition.

Summarizing, at step a) an amorphous oxide with very small particle size ( $<1.5$  nm) is formed (see Figure 2.a), at step b) a crystalline oxide solid solution is formed with a particle size around 5 nm (see Figure 2.b), and at step c) (see Figure 2.c) a single metallic phase is obtained (particle size 10-20 nm).

#### Example 2

##### Temperature Programmed Reduction (TPR) on NiO, CuO and NiCuO<sub>x</sub> oxides

TPR experiments were carried out in a tubular quartz microreactor. A temperature sweep rate of  $10\text{ }^{\circ}\text{C min}^{-1}$  was selected, the catalyst weight was 5 mg and a TCD detector was used to determine H<sub>2</sub> consumption. A stream of 5% H<sub>2</sub> in Ar at a flow rate of 30 ml/min was fed to the reactor.

Three different samples, CuO (Aldrich), NiO (Aldrich) and Ni<sub>0.58</sub>Cu<sub>0.42</sub>O<sub>x</sub> were subjected to TPR experiments with H<sub>2</sub>, in order to compare their reduction kinetics and confirm the effectiveness of the process of the invention in preparing a metallic alloy.

The recorded profiles of Figure 3 show that the onset for hydrogen consumption and the respective peak maximum did occur on the mixed phases at a much lower temperatures with respect to the single phases: 470 K (about 197°C) for Ni<sub>0.58</sub>Cu<sub>0.42</sub>O<sub>x</sub>, 503 K (about 230°C) for CuO and 626 K (about 353°C) for NiO, respectively. Further, the reduction peak for the mixed

$\text{Ni}_{0.58}\text{Cu}_{0.42}\text{O}_x$  phases is much more narrow, pointing for a faster reduction kinetics, thus a higher affinity for hydrogen, effective for reforming.

### Example 3

#### Catalytic activity for methane oxidation (reforming)

5 Methane reforming experiments were carried out in a packed bed tubular reactor (in-house made), where 15 mg of alloy catalyst of example 1,c) were diluted in 50 mg of quartz powder (Carlo Erba). Reactant feed was  $\text{H}_2\text{O}/\text{CH}_4$  (molar ratio 4:1), with a space velocity of  $10^5 \text{ h}^{-1}$ .

10 Methane steam reforming experiments were carried out on a  $\text{Ni}_{0.58}\text{Cu}_{0.42}$  bulk alloy example 1,c) and on a Ni,Cu metallic mixture of same compositions prepared by grinding and ultrasonically mixing NiO and CuO oxides (Aldrich) followed by reduction under same conditions of Example 1,c).

15 Figure 4 shows that the onset temperature for the reaction on the  $\text{Ni}_{0.58}\text{Cu}_{0.42}$  alloy is significantly lower than for that on the Ni,Cu metallic mixture. The inflection point in the curve of catalytic activity vs. temperature for  $\text{Ni}_{0.58}\text{Cu}_{0.42}$  alloy is about 50 K ( $200^\circ\text{C}$ ) lower than that of Ni,Cu metallic mixture and 100 K lower than that reported in the literature for supported Ni catalysts (see C.T Au, H.Y. Wang, H.C. Wan, J. Catalysis 158 (1996) 343).

20 Elemental analysis was used to determine the carbon content in the catalyst after catalytic and electrochemical experiments. Analyses were carried out with a Carlo Erba CHNSO elemental analyser. No evidence of carbon deposition was found after reforming experiments on the  $\text{Ni}_{0.58}\text{Cu}_{0.42}$  alloy.

### Example 4

#### $\text{Ni}_{0.58}\text{Cu}_{0.42}$ -CGO (50:50 w/w) cermet preparation

25  $\text{Ce}_{0.9}\text{GdO}_{1.95}$  (CGO) (prepared by co-precipitation of the cerium and gadolinium nitrates with oxalic acid at pH=6, followed by thermal decomposition at 973K, as from Herle J.V., Horita T., Kawada T., Satoi N., Yokokawa H., Dokya M., Ceramic International, vol. 24, 229, 1998), and amorphous  $\text{Ni}_{0.58}\text{Cu}_{0.42}\text{O}$  (obtained in Example 1,a) were intimately mixed in an agate mortar. Slurry was prepared by adding 10 ml of isopropyl alcohol to the powder mixture (116 mg CGO and 147 mg of amorphous  $\text{Ni}_{0.58}\text{Cu}_{0.42}\text{O}$ ), which

30

was further ultrasonicated in order to reduce the formation of agglomerates. The composite was then heated to 423 K (about 150°C) for solvent evaporation, followed by reduction at 773 K (about 500°C) for 0.5 h under hydrogen flux. The formation of the NiCu alloy on CGO was confirmed by X-ray diffraction (see Figure 5 wherein \* is for  $\text{Ni}_{0.58}\text{Cu}_{0.42}$ , and ° is for CGO).

#### Example 5

##### Preparation of a $\text{Ni}_{0.5}\text{Cu}_{0.5}$ -CGO (50 :50 w/w) cermet (reference preparation)

1g of CGO powder was impregnated according to what taught by H. Kim, et al., *supra*, with a 50 ml aqueous solution of  $\text{Cu}(\text{NO}_3)_2 \cdot \text{H}_2\text{O}$  (280 mg) and  $\text{Ni}(\text{NO}_3)_2 \cdot \text{H}_2\text{O}$  (310 mg). Finally the layer was again heated to 500°C and reduced in flowing  $\text{H}_2$  at 900°C.

XRD analysis showed (Figure 6) that the NiCu/CGO cermet prepared according to said method show particle size higher and surface area lower than that obtained in Example 4 (as from comparison with Figure 5). Table 2 sets forth the comparison by numbers.

Table 2

Particle size (d) and surface area (MSA) of NiCu alloys in NiCu-CGO cermets

Preparation process	d / nm	Surface area ( $\text{m}^2/\text{g}$ )
Example 4	15	43
Example 5	26	26

#### Example 6

##### Cell preparation

A cell was fabricated having a CGO electrolyte, a LSM/CGO layer as a cathode and a NiCu-CGO layer of Example 4 as an anode.

The CGO electrolyte (~500  $\mu\text{m}$ , >90% theoretical density) was prepared by uniaxial pressing at 300 MPa of a  $\text{Ce}_{0.9}\text{Gd}_{0.1}\text{O}_{1.95}$  powder obtained as in Example 4. Before use for pellet preparation, the powder was thermally treated at 1050°C for 1 h. The pellet was thermally treated at 1550°C for 3 hrs.

As the cathode, a 30  $\mu\text{m}$  LSM/CGO layer (50:50%wt) was deposited by a painting process on one side of the pellet and fired at 1250°C for 1 hour in air to assure good bonding to the electrolyte. The slurry used was composed of 100 mg CGO synthesized powder and 100 mg LSM ( $\text{La}_{0.6}\text{Sr}_{0.4}\text{MnO}_3$ , Praxair) both intimately mixed and dispersed in 1.5 ml of isopropanol.

A 20  $\mu\text{m}$  anodic cermet layer of amorphous  $\text{Ni}_{0.58}\text{Cu}_{0.42}\text{O}$ -crystalline CGO (50:50%wt) slurry was deposited by painting in one step on the CGO dense layer side of the CGO-LSM/CGO substrate. The slurry was prepared by dispersing 100 mg of amorphous  $\text{Ni}_{0.58}\text{Cu}_{0.42}\text{O}_x$  and 100 mg of synthesized CGO powders in 1.5 ml of isopropylalcohol (carlo Erba). The total amount of deposited metal phase was 2.5  $\text{mg}/\text{cm}^2$ . This was dried at 423 K (about 150°C) to remove the solvent.

A 5  $\mu\text{m}$  Au (Hereus) film, to be used as the anodic current collector in the electrochemical cell, was then deposited by painting on the anodic layer, and the whole assembly was heated at 150°C for solvent evaporation. Two Au wires on each side were allocated for sampling current and potential.

Also, a 5  $\mu\text{m}$  thin Pt (Engelhard) film, to be used as the cathodic current collector in the electrochemical cell, was then deposited by painting on the cathodic layer. A Pt reference electrode was allocated on the cathodic side to allow operation of the device under half-cell configuration.

The cell (0.5  $\text{cm}^2$  active area) was mounted on an alumina tube and sealed with quartz adhesive.

Finally the system was heated at 500°C for 1h in air to allow formation of a crystalline  $\text{Ni}_{0.58}\text{Cu}_{0.42}\text{O}_x$  oxide. Inert gas (He) was passed through the anode before hydrogen supply. An hydrogen stream flow rate (50  $\text{cc min}^{-1}$ ) was fed to the anode at 500°C to assure the alloy formation.

#### Example 7

##### Characterization in half-cell configuration (hydrogen fuelled anode)

Electrochemical evaluation of the performance of a solid oxide fuel cell according to Example 6, fed with hydrogen was carried out.

The hydrogen flow rate was  $50 \text{ cc min}^{-1}$ , and static air was used as oxidant. No humidification was used for the anode stream.

The cell was conditioned for at least 1 h in hydrogen at  $800^\circ\text{C}$  before recording the polarization curves and ac-impedance spectra.

5 Electrochemical experiments were carried out both under galvanostatic and potentiostatic controls by using an AUTOLAB Ecochemie potentiostat/galvanostat and impedance analyser. The polarization data were collected under steady state conditions. Ac-impedance spectra were collected in the range  $1 \text{ MHz}$ - $1 \text{ mHz}$  with a  $20 \text{ mV}$  rms sinusoidal signal under open circuit  
10 conditions. A four-electrode configuration was used in all cases. In half-cell experiments, one potential probe was connected to a non-polarized reference electrode and the overpotential of the working electrode was measured against this reference.

Raw half-cell data of the  $\text{Ni}_{0.58}\text{Cu}_{0.42}\text{O}/\text{CGO}$  cermet anode/CGO electrolyte interface indicated that this anode is active for the electrochemical oxidation of dry  $\text{H}_2$ , as depicted in Figure 7.

IR-free data (Figure 8) show very low overpotentials, less than  $50 \text{ mV}$  for  $j = 500 \text{ mA cm}^{-2}$ . The curves recorded in presence of hydrogen show no activation (kinetic) control. These data indicate that the  $\text{Ni}_{0.58}\text{Cu}_{0.42}/\text{CGO}$  cermet anode combined with thin CGO electrolyte achieves high performances  
20 for the oxidation of dry hydrogen.

#### Example 8

##### Characterization in half-cell configuration (dry methane fuelled anode)

Electrochemical evaluation of the performance of a solid oxide fuel cell according to Example 6, fed with hydrogen was carried out.

Methane flow rate was  $50 \text{ cc min}^{-1}$ , and static air was used as oxidant. No humidification was used for the anode stream.

The cell was conditioned for at least 1 h in methane at  $800^\circ\text{C}$  before recording the polarization curves and ac-impedance spectra.

Electrochemical experiments were carried out as in Example 8, but testing the cell at three different temperatures, i.e. 800°C, 700°C and 600°C, sequentially.

Raw half-cell data of the  $\text{Ni}_{0.58}\text{Cu}_{0.42}\text{O}/\text{CGO}$  cermet anode/CGO electrolyte interface indicated that this anode is active for the electrochemical oxidation of dry methane, as depicted in Figure 7.

IR-free data (8) show for  $j = 500 \text{ mA cm}^{-2}$  overpotentials of 250 and 350 mV vs. the reversible potential for  $\text{H}_2$  oxidation at 800°C and 700°C respectively. The curves recorded in presence of methane show a slight activation (kinetic) control that is not observed in presence of hydrogen. These data indicate that the  $\text{Ni}_{0.58}\text{Cu}_{0.42}/\text{CGO}$  cermet anode combined with thin CGO electrolyte achieve high performances for the oxidation of dry methane.

#### Example 9

##### Analysis of morphology and carbon deposition characteristics of the anodic cermet

The overall process of formation of the  $\text{Ni}_{0.58}\text{Cu}_{0.42}$  alloy/CGO cermet in a cell prepared according to Example 6, and the modifications occurring after its exposure to dry methane, according to Example 8 under electrochemical operation conditions were investigated by SEM (scanning electron microscopy), and TEM (transmission electron microscopy) analyses. SEM analysis (Figure 9) shows uniform porosity of the anodic layer (upper part in the figure, on the membrane layer) during the preparation steps and after operation in the fuel cell. Further insights on the morphology were obtained by TEM analysis.

Distinction between  $\text{Ni}_{0.58}\text{Cu}_{0.42}\text{O}$  (or  $\text{Ni}_{0.58}\text{Cu}_{0.42}$  alloy) and CGO phases was possible by observing the lattice planes at high magnification which are quite different in spacing between the two phases (Figure 10a).

TEM analysis of the amorphous  $\text{Ni}_{0.58}\text{Cu}_{0.42}\text{O}$ -crystalline CGO cermet precursors clearly indicates a significant difference in terms of particle sizes between the two phases. After thermal treatment in air at 500°C, the  $\text{Ni}_{0.58}\text{Cu}_{0.42}\text{O}$  phase became crystalline but there was only a slight increase in

the particles size associated to this phase which are surrounding the larger CGO crystals (Figure 10b). After thermal reduction and subsequent operation under fuel cell conditions, the dimension of  $\text{Ni}_{0.58}\text{Cu}_{0.42}$  and CGO particles became similar (Figure 11), these particles join together maximizing the interface characteristics. It has been demonstrated that the present invention allows a superior extension of the three-phase boundary zone.

After operation of the anodic cermet at 800°C under SOFC conditions with a current density of 250 mA cm<sup>-2</sup> for 20 hrs, no evidence of carbon formation was observed by TEM on the surface of the alloy particles, as from Figure 11.

Another cell, analogously prepared, was operated at 700°C for 50 hours. Also in this case no evidence of carbon deposition was detected by TEM.

This result is opposite of that reported in Kim H., Lu C., Worrell W.L., Vohs J.M., Gorte R.J., J. Electrochem. Soc., 149 (3) A247-A250 (2002) indicating a significant carbon deposition in the same time interval for an impregnated NiCu alloy layer under SOFC operation at 800 °C.

The cermet anode of the present invention is able to make the solid oxide fuel cell comprising it to operate with a wide selection of fuels. Especially said cermet, thanks to its characteristics of ionic and electronic conductivity, and surface area and catalytic activity, permits the use of dry methane as fuel for electrochemical apparatus, without any sign of carbon deposition.

## CLAIMS

1. Solid oxide fuel cell including
  - a cathode;
  - at least an electrolyte membrane, and
  - 5 - an anode comprising a ceramic material and an alloy comprising nickel and at least a second metal selected from aluminium, titanium, molybdenum, cobalt, iron, chromium, copper, silicon, tungsten, niobium, said alloy having an average particle size not higher than 20 nm.
- 10 2. Solid oxide fuel cell according to claim 1 wherein said alloy has an average particle size not higher than 16 nm.
3. Solid oxide fuel cell according to claim 1 wherein said alloy has a mean surface area higher than 20 m<sup>2</sup>/g.
4. Solid oxide fuel cell according to claim 3 wherein said alloy has, a mean
- 15 surface area higher than 30 m<sup>2</sup>/g.
5. Solid oxide fuel cell according to claim 4 wherein said alloy has, a mean surface area higher than 40 m<sup>2</sup>/g.
6. Solid oxide fuel cell according to claim 1 wherein said alloy has a second metal content of from 1% by weight to 99% by weight.
- 20 7. Solid oxide fuel cell according to claim 6 wherein said alloy has a second metal content of from 30% by weight to 70% by weight.
8. Solid oxide fuel cell according to claim 7 wherein said alloy has a second metal content of from 40% by weight to 60% by weight .
9. Solid oxide fuel cell according to claim 1 wherein said alloy has a nickel
- 25 content of from 1% by weight to 99% by weight.
10. Solid oxide fuel cell according to claim 6 wherein said alloy has a nickel content of from 30% by weight to 70% by weight.
11. Solid oxide fuel cell according to claim 7 wherein said alloy has a nickel content of from 40% by weight to 60% by weight .
- 30 12. Solid oxide fuel cell according to claim 1 wherein said second metal is copper.

13. Solid oxide fuel cell according to claim 1 wherein said ceramic material is selected from yttria-stabilized zirconia (YSZ), cerium gadolinium oxide (CGO), samarium-doped ceria (SDC), mixed lanthanum and gallium oxides.

14. Solid oxide fuel cell according to claim 1 wherein said ceramic material has a particle size not higher than 50 nm.

15. Solid oxide fuel cell according to claim 1 wherein said ceramic material has a particle size from 1 nm to 25 nm.

16. Solid oxide fuel cell according to claim 1 wherein said ceramic material is doped with at least one cation selected from calcium, magnesium, strontium, lanthanum, yttrium, ytterbium, neodymium and dysprosium.

17. Solid oxide fuel cell according to claim 13 wherein said ceramic material is cerium gadolinium oxide (CGO).

18. Solid oxide fuel cell according to claim 1 performing in substantially dry hydrocarbon.

19. Cermet comprising a ceramic material and an alloy having a particle size not higher than 20 nm.

20. Process for preparing a cermet including a ceramic material and a metallic material comprising an alloy comprising nickel and at least a second metal selected from aluminium, titanium, molybdenum, cobalt, iron, chromium, copper, silicon, tungsten, niobium, said process comprising the steps of:

- a) producing a precursor of the metallic material;
- b) producing the ceramic material;
- c) combining said precursor and ceramic material to obtain a composite
- d) reducing said composite

wherein step a) comprises the phases of

- a-1) dissolving a hydrosoluble salt of Ni and a hydrosoluble salt of a second metal in water;
- a-2) adding a chelating agent to the solution resulting from step a-1);
- a-3) adding an oxidizing agent to the solution resulting from step a-2);
- a-4) isolating said precursor.

21. Process according to claim 20 wherein step b) comprises the phases analogous to those from a-1) to a-4).

22. Process according to claim 20 comprising the phases of adjusting the pH of the solution resulting from phase a-2) at a value higher than about 5.

5 23. Process according to claim 20 wherein phase d) is carried out with hydrogen at a temperature ranging between about 400°C and about 1000°C.

24. Method for producing energy comprising the steps of:

10 - feeding at least one fuel into an anode side of a solid oxide fuel cell comprising an anode comprising a ceramic material and an alloy comprising nickel and at least a second metal selected from aluminium, titanium, molybdenum, cobalt, iron, chromium, copper, silicon, tungsten, niobium, a cathode and at least an electrolyte membrane disposed between said anode and said cathode;

15 - feeding an oxidant into a cathode side of said solid oxide fuel cell; and  
- oxidizing said at least one fuel in said solid oxide fuel cell, resulting in production of energy.

25. Method according to claim 24 wherein the at least one fuel is hydrogen.

26. Method according to claim 24 wherein the at least one fuel is an alcohol.

20 27. Method according to claim 24 wherein the at least one fuel is a hydrocarbon in gaseous form.

28. Method according to claim 27 wherein the hydrocarbon is substantially dry.

29. Method according to claim 24 wherein the at least one fuel is a hydrocarbon in liquid form.

25 30. Method according to claim 24 wherein the at least one fuel is substantially dry methane.

31. Method according to claim 24 wherein the fuel is internally reformed in the anode side.

30 32. Method according to claim 24 wherein the solid oxide fuel cell operates at a temperature ranging between from 500°C and 800°C.

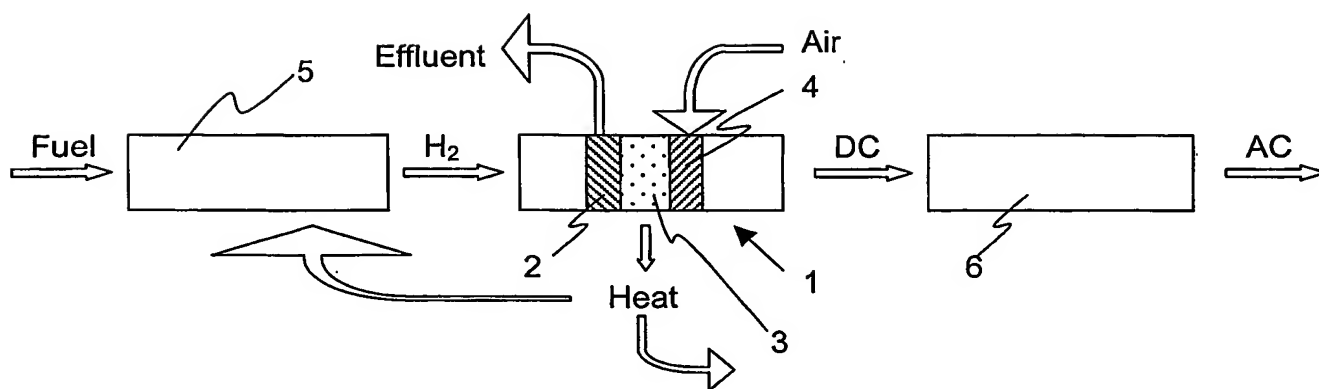


Figure 1a

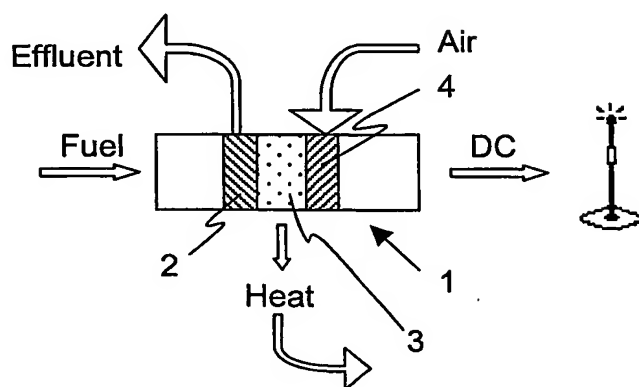


Figure 1b

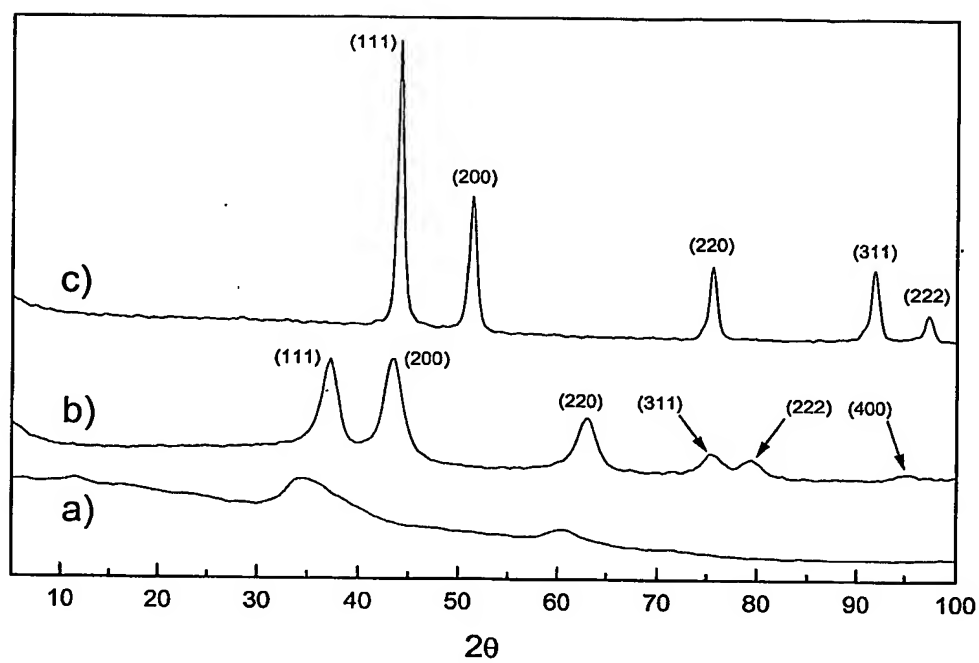


Figure 2

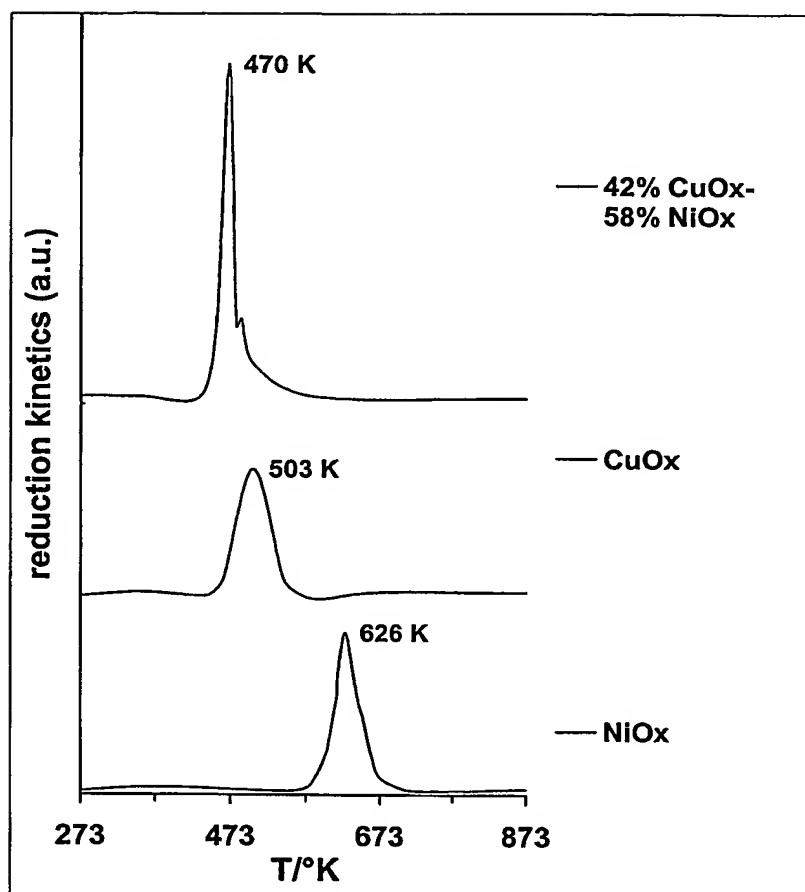


Figure 3

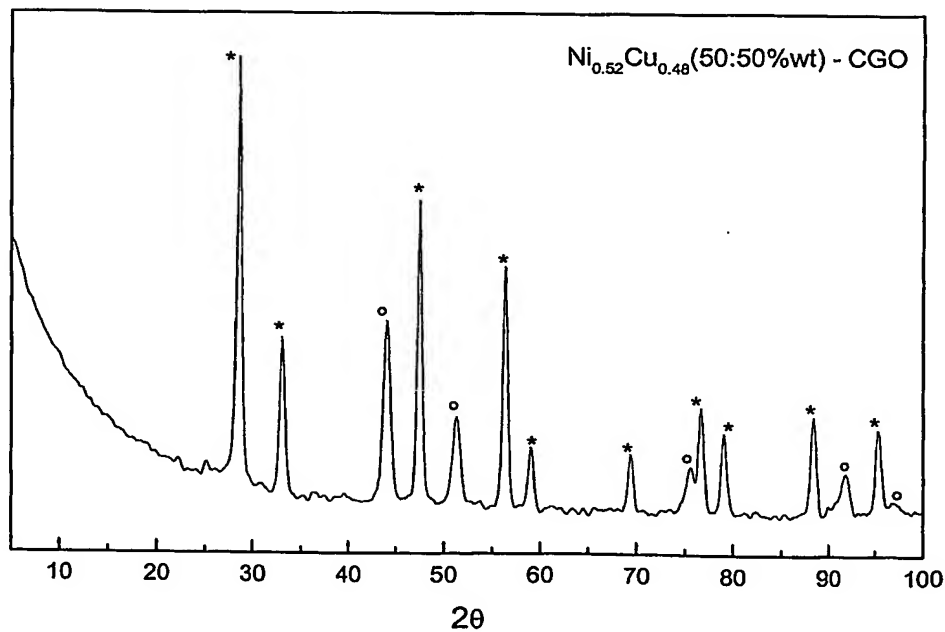
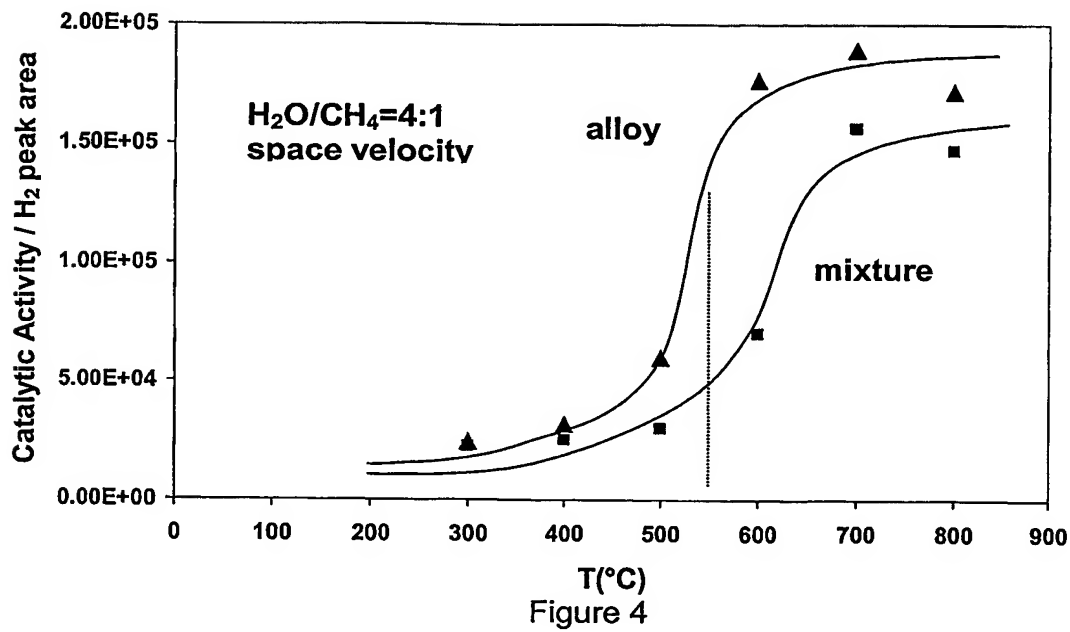


Figure 5

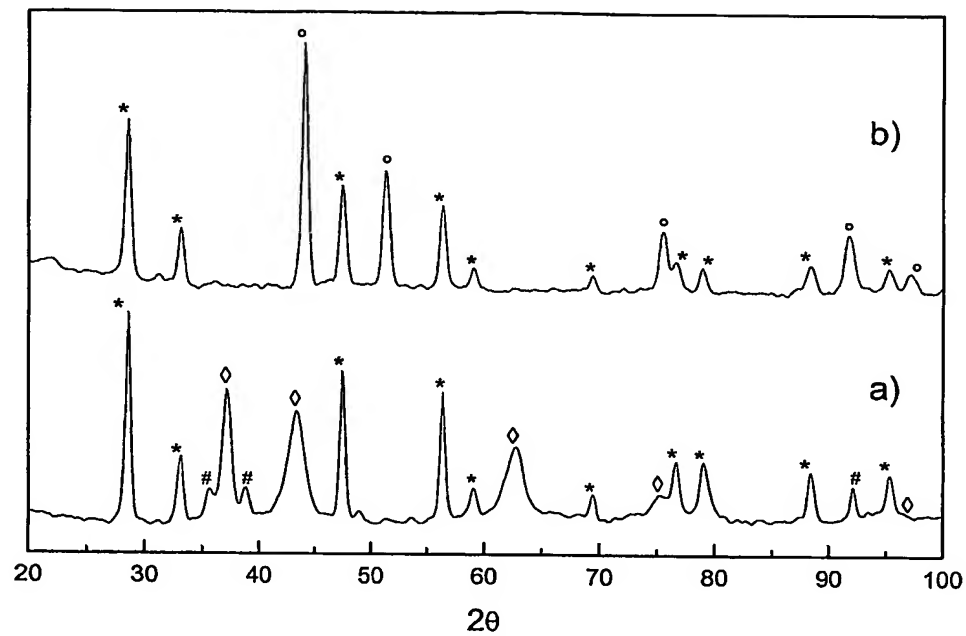


Figure 6

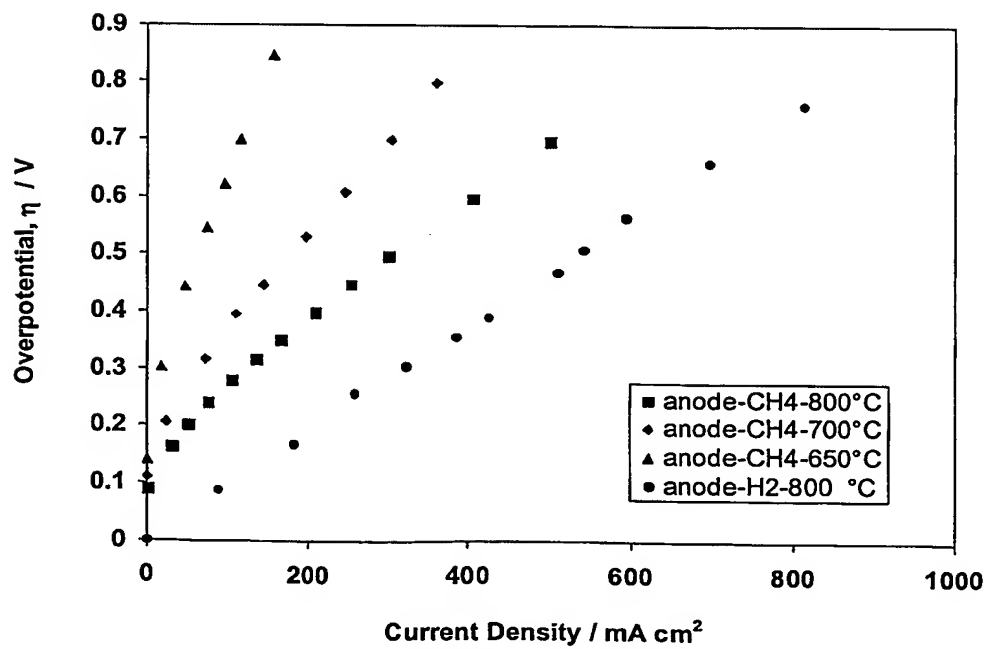


Figure 7

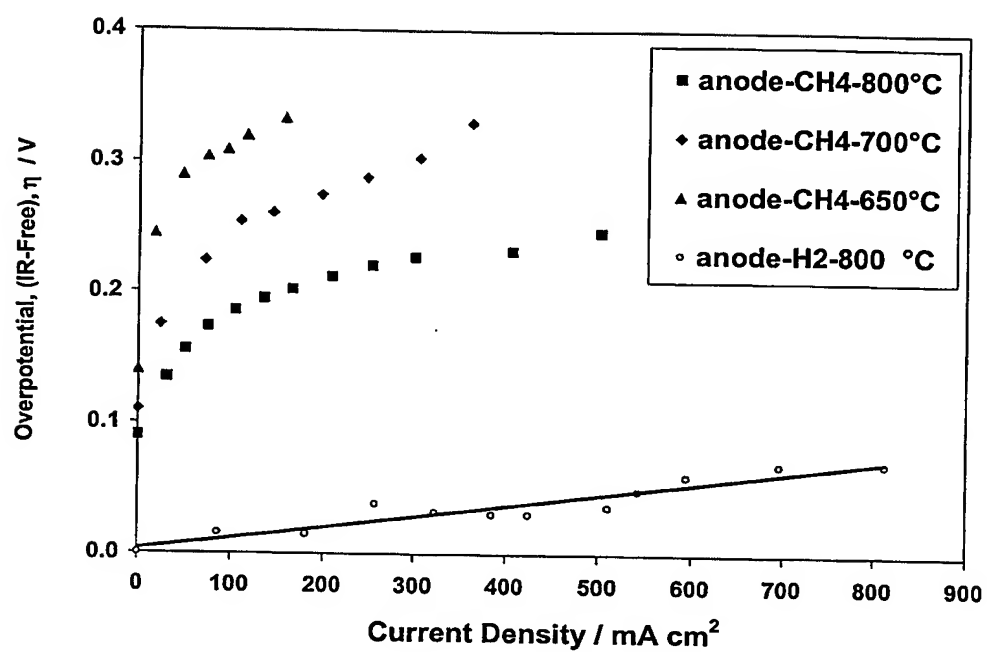


Figure 8

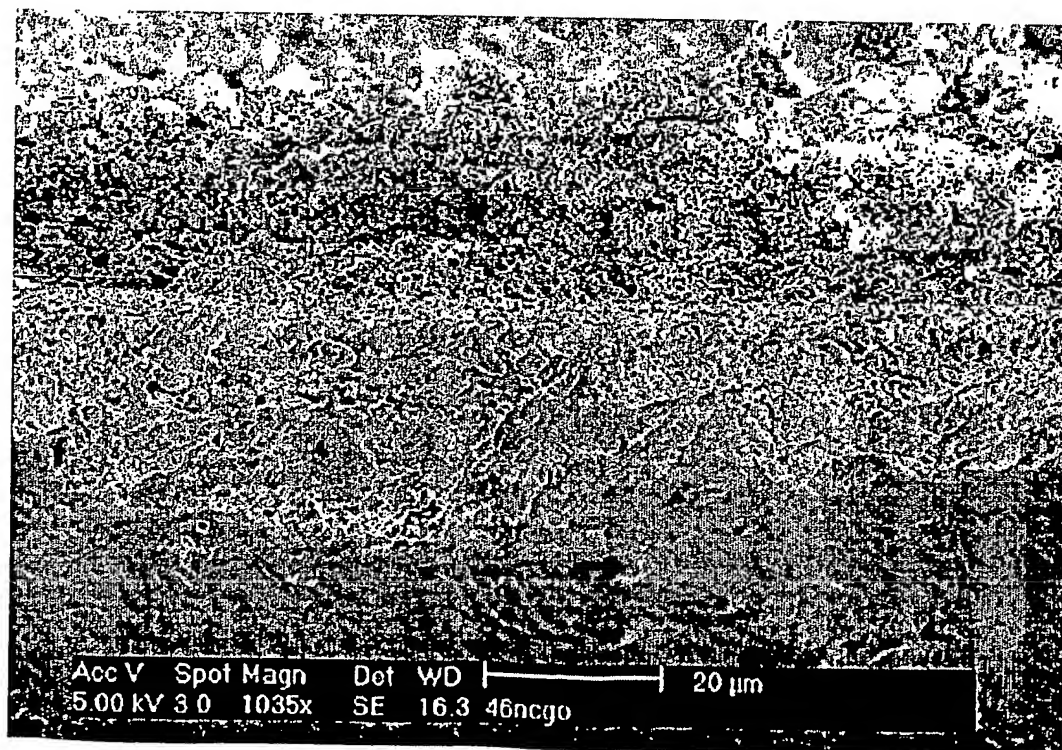


Figure 9

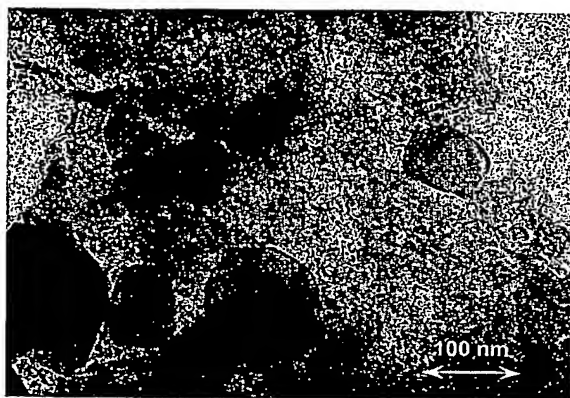


Figure 10a

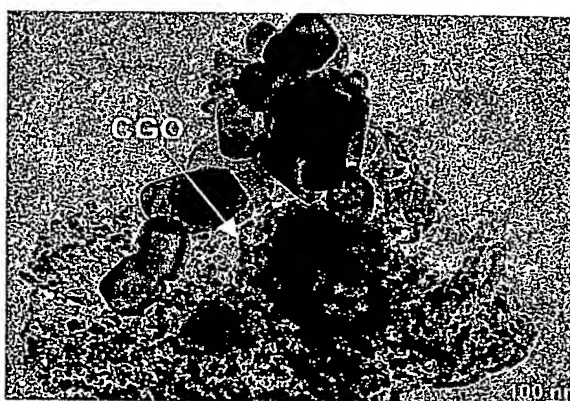


Figure 10b

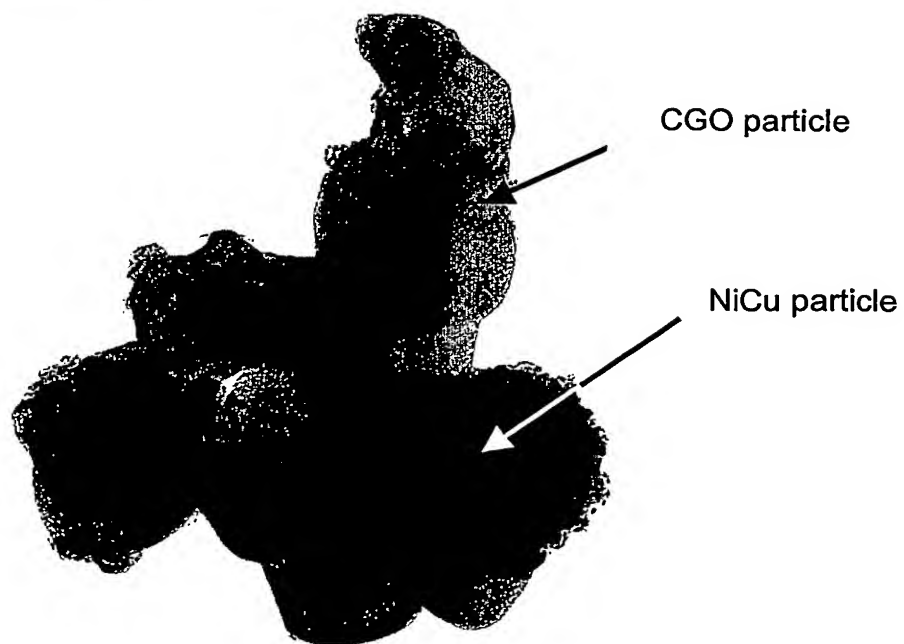


Figure 11

# INTERNATIONAL SEARCH REPORT

International Application No

PCT/EP 03/11639

## A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 H01M8/22 H01M8/12 H01M4/86

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 H01M

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, PAJ, WPI Data, CHEM ABS Data

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	<p>KIM H ET AL: "CU-NI CERMET ANODES FOR DIRECT OXIDATION OF METHANE IN SOLID-OXIDE FUEL CELLS"</p> <p>JOURNAL OF THE ELECTROCHEMICAL SOCIETY, ELECTROCHEMICAL SOCIETY. MANCHESTER, NEW HAMPSHIRE, US,</p> <p>vol. 149, no. 3,</p> <p>29 January 2002 (2002-01-29), pages A247-A250, XP001157413</p> <p>ISSN: 0013-4651</p> <p>cited in the application</p> <p>* see p. A247, right col. *</p> <p>the whole document</p> <p style="text-align: center;">---</p> <p style="text-align: center;">-/--</p>	1-32

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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Date of the actual completion of the international search

5 February 2004

Date of mailing of the international search report

16/02/2004

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2  
NL - 2280 HV Rijswijk  
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,  
Fax: (+31-70) 340-3016

Authorized officer

Stellmach, J

# INTERNATIONAL SEARCH REPORT

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PCT/EP 03/11639

## C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	<p>GORTE, R.J. ET AL.: "Anodes for direct Oxidation of dry hydrocarbon in a Solid-Oxide Fuel Cell"</p> <p>ADV. MATERIALS, vol. 12, no. 19, 2 October 2000 (2000-10-02), pages 1465-1469, XP001153929</p> <p>WEINHEIM cited in the application * see p.1469, left col. lines 5-15 * the whole document</p>	1-32
Y	<p>WO 00 52780 A (VOHS JOHN M ; CRACIUN RADU (US); GAS RES INST (US); GORTE RAYMOND J) 8 September 2000 (2000-09-08) cited in the application * see p.4, 1.13-26; p.9, 1.3-7 ; claims 15-19 * the whole document</p>	1-32
Y	<p>MURRAY, E.P. ET AL.: "A direct methanol fuel cell with a ceria-based anode"</p> <p>NATURE, vol. 400, 12 August 1999 (1999-08-12), pages 649-651, XP002249450 * see p.651 * the whole document</p>	1-32
Y	<p>LIVERMORE S J A ET AL: "Fuel reforming and electrical performance studies in intermediate temperature ceria-gadolinia-based SOFCs"</p> <p>JOURNAL OF POWER SOURCES, ELSEVIER SEQUOIA S.A. LAUSANNE, CH, vol. 86, no. 1-2, March 2000 (2000-03), pages 411-416, XP004194152 ISSN: 0378-7753 cited in the application * see p.415, right col., summary *</p>	1-32
Y	<p>PARK, S. ET AL.: "Direct Oxidation of Hydrocarbons in a Solid Oxide Fuel Cell. I. Methane Oxidation"</p> <p>J. ELECTROCHEM-SOC., vol. 146, no. 10, 1999, pages 3603-3605, XP009014798 * see p.3603, left col., last par. * the whole document</p>	1-32
Y	<p>WO 97 35349 A (BADWAL SUKHVINDER P S ; JAFFREY DON (AU); NEWMAN JOHN (AU); FOGER K) 25 September 1997 (1997-09-25) * see p.2, 1.18-24, claims 1, 2 and 11 * the whole document</p>	1-32

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## INTERNATIONAL SEARCH REPORT

International Application No

PCT/EP93/11639

## C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 5 656 387 A (BARNETT SCOTT ALEXANDER ET AL) 12 August 1997 (1997-08-12) * see col 1, l. 19-59, claim 1 * the whole document ----	1-32
Y	PARK, S. ET AL: "Direct Oxidation of hydrocarbons in a solid-oxide fuel cell" NATURE, vol. 404, 16 March 2000 (2000-03-16), pages 265-267, XP002249578 * see p.265, left col, penultimate par. * the whole document -----	1-32
Y	EP 0 588 536 A (CERAMATEC INC) 23 March 1994 (1994-03-23) * see p.3, l. 6-22, claims 1-7 * the whole document -----	1-32

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Information on patent family members

International Application No

PCT/JP03/11639

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
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